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FLAME PROPAGATION LIMITS OF PROPANE AND n-PENTANE  
IN OXIDES OF NITROGEN

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## SUMMARY

Flame propagation limits of propane and n-pentane in oxides of nitrogen were obtained at subatmospheric pressures in a 2-inch-diameter by 48-inch-length tube. Three oxidants were investigated, namely, nitric oxide NO, nitrogen tetroxide  $N_2O_4$ , and a nearly equimolar mixture of these two oxides.

Flames propagated through all the fuel-oxidant mixtures with the limits occurring at equivalence ratios of roughly  $1/3$  and 3.

The minimum propagation pressure of the fuel-NO mixtures in the 2-inch-diameter tube was appreciably greater than that of the fuel- $N_2O_4$  mixtures. The limits of the nitrogen oxides with propane at 1 atmosphere were narrower on a stoichiometric basis than for equivalent propane mixtures with molecular oxygen and nitrogen, interpolated from published data.

Estimated flame temperatures at the lean limit were appreciably lower for the  $N_2O_4$  and the NO- $N_2O_4$  mixtures than for the NO mixtures and were about the same as lean-limit temperatures of fuel-air mixtures. In general, the data attest to the relative chemical stability of NO in the hydrocarbon flames.

## INTRODUCTION

From the practical standpoint, the engineer should know flame propagation limits in order to design combustors and specify pressures, compositions, and temperatures in which a given gaseous fuel-oxidant combination will burn. He can also use the data to design against unwanted burning or explosions. From the theoretical standpoint, flame propagation limits are important because they can be correlated with other combustion parameters and thus aid in the fundamental understanding of combustion (e.g., ref. 1).

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In the rocket field, there is a need for fuel-oxidant combinations which can be stored and are cheap. A good answer is hydrocarbon fuels from petroleum and oxidants derived from nitric oxide NO. The oxidants, nitrogen tetroxide  $N_2O_4$ , mixtures of  $N_2O_4$  and NO, and fuming nitric acids that may contain excess  $N_2O_4$  are of interest. Since rockets may have to start at high altitudes, data on rocket propellants should include flame propagation limits at low pressures.

The great mass of existing combustion work has been in atmospheres of air. Less work has been done with undiluted oxygen and still less with oxidizing atmospheres that contain no free oxygen. Flame-speed determinations and spectrographic studies have recently been made of several fuels burning in atmospheres of nitrous oxide  $N_2O$ , nitric oxide NO, nitrogen tetroxide  $N_2O_4$ , and nitric acid vapor (refs. 2 and 3); flammability limit data (reviewed in ref. 4) have been obtained with various low molecular weight fuels in  $N_2O$  and NO, usually in tubes of small diameter. The limits at a pressure of 1 atmosphere, for propane- $N_2O_4$ -air are also available (ref. 5).

These data for the most part, however, do not cover rocket propellants. A study of flame propagation limits of hydrocarbons with NO,  $N_2O_4$ , and NO- $N_2O_4$  at subatmospheric pressures would fill an engineering need, and it would also extend basic combustion data to a little-explored class of fuel-oxidant mixtures. Therefore, the flame propagation limits of several gaseous hydrocarbon - nitrogen oxide mixtures were studied at the NACA Lewis laboratory, and the results are reported herein.

The experiments were conducted in a standard apparatus (ref. 4), except that the tube was closed at the lower end to permit determinations at low pressures as in references 6 to 8. In some cases, motion pictures and rapid-response pressure records were also made.

Two types of information are obtained with this apparatus. At pressures near atmospheric, the composition limits approach physical-chemical constants independent of apparatus. At lower pressures, the limits are dependent upon tube diameter. The diameter is simply related to parallel-plate quenching distance. For several hydrocarbon-oxygen-nitrogen mixtures, the limiting pressure at constant composition is nearly inversely proportional to the tube diameter or the parallel-plate quenching distance (refs. 1, 9, and 10). Since a constant tube diameter was used in the present work, a similar dependence of limiting pressure on tube diameter must be assumed if the data at lower pressures are to be applied to other equipment.

## PROCEDURE

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Apparatus. - The apparatus (fig. 1) consisted of a vertical flame tube (2-in. I.D. by 48-in. length) and the equipment necessary to prepare and store a mixture of the gases. The apparatus was pyrex glass throughout. The ground-glass seals and bearings were lubricated with halocarbon grease. Mixtures were prepared in a 50-liter flask with a glass stirrer revolved by an electrically driven pantograph-type linkage; a ball-and-socket joint served as a bearing and seal for the stirrer. A mercury manometer was used to measure the pressure of the gases in the reservoir during mixture preparation and in the flame tube during propagation experiments. The design of the manometer permitted frequent cleaning of the mercury well, since mercury is attacked by  $N_2O_4$ . A 1-liter-gas burette was provided for the measurement of small increments of propane. The displacement fluid in the burette was a 50 percent by weight solution of sodium hydroxide (vapor pressure,  $\approx 1$  mm). The propane passed through a drying tower of anhydrous calcium sulfate between the burette and the reservoir. A specially constructed flask was used for drying, weighing, and transferring liquid  $N_2O_4$ . The gas reservoir and the mixing and measuring equipment were all contained in an insulated box. For explosion protection, two of the sides and the top and the bottom of the box were made of steel plate. The manometer and the gas burette were read through a thick, laminated glass window. The flame tube was mounted behind a laminated glass window in a ventilated cabinet closed with a clear plastic door. The tube was surrounded by two annular air jackets. Temperatures were measured by three mercury thermometers placed next to the tube inside the inner jacket. The spread in the three temperatures was usually less than  $2^\circ C$ .

The ignition source was a 25,000-volt, 60-cycle spark at the bottom of the tube between pointed electrodes of 1.5-millimeter-diameter stainless steel wire. With propane in air and propane in nitric oxide, a  $3/4$ -inch gap was used. In all subsequent experiments, a  $5/8$ -inch gap was used, because the  $3/4$ -inch gap was too large at the higher pressures for a 25,000-volt discharge through mixtures containing large amounts of  $N_2O_4$ . The power input to the spark transformer varied from 275 to 330 watts; the power increased as the pressure increased in the tube.

Some auxiliary equipment was also used. Motion pictures were made directly from the light of the flames at 24 frames per second using a 16-millimeter camera. The pressure, from a strain-gage pickup registering on a cathode-ray oscilloscope, was recorded with a strip-film camera. The cameras were driven electrically through a time-delay switch.

Fuels and oxidants. - The fuels and oxidants were purchased from commercial sources. The specified purities of the propane and  $n$ -pentane were 99.9 and 99 percent, respectively. A laboratory determination of the  $N_2O_4$

gas, as it issued from the weighing bottle containing phosphorus pentoxide,  $P_2O_5$ , was substantially 100 percent pure. Colormetric comparisons of the NO gas showed it contained less than 1 percent by weight  $N_2O_4$ ; this was not included in the composition calculations.

Preparation of mixtures. - The first mixture of each series was prepared by admitting to the reservoir, in this order, fuel, NO, and  $N_2O_4$ , as required. The pressures and temperatures were recorded after the mixing process. As a secondary check, the  $N_2O_4$  (dried over  $P_2O_5$ ) was weighed. Before each mixture preparation, the reservoir was evacuated and flushed with fuel.

Subsequent mixtures in a series were made by either adding more oxidant or more fuel, depending on which was most convenient and accurate. The propane and n-pentane with NO and the propane with  $N_2O_4$  mixtures were varied by adding more of the oxidant. Mixtures of either hydrocarbon with NO- $N_2O_4$  and n-pentane with  $N_2O_4$  were changed by adding more of the hydrocarbon. Increments of propane were admitted as gas; when the increments were small they were measured directly with the gas burette. Increments of n-pentane were admitted as a liquid through a pressure-lock system; the volume of the liquid was measured.

The primary measurements used in the calculation of the mixture compositions were the pressures read from the mercury manometer except when the hydrocarbon increments were measured directly either as gas or liquid.

Calculation of mixture composition. - The hydrocarbon-NO mixtures were calculated directly from the partial pressures assuming ideal gas behavior. In mixtures containing  $N_2O_4$ , however, a Newton-Raphson iteration procedure (e.g., ref. 11) was used. Data used in these computations were (1) partial pressure and temperature of the fuel and NO (when used), (2) equilibrium pressure and temperature after  $N_2O_4$  was added, and (3) equilibrium constants for  $N_2O_4 \rightleftharpoons 2 NO_2$  (ref. 12) and  $NO + NO_2 \rightleftharpoons N_2O_3$  (ref. 13). Pressures were measured directly in the first mixture of each series and calculated in subsequent mixtures. The accuracy of the nominal mixture composition (other than the initial mixture) depends not only upon the precision of the pressure measurements and the closeness with which the gases follow the ideal gas laws but also on the number of additions in a given series and (in mixtures containing  $N_2O_4$ ) the accuracy of the equilibrium data.

The equilibria are the largest source of uncertainty. Although the dissociation  $N_2O_4 \rightleftharpoons 2 NO_2$  has been studied over many years, complete agreement was not found in the literature. In order to help in the

3697 selection of suitable constants, some experimental constants were calculated from the data of these experiments. The trend was intermediate between the constants of references 12 and 14. The data of reference 12 were selected primarily for the sake of consistency with other experimental work. The constants for the formation of  $N_2O_3$  (ref. 13) and the volume limits of propane- $N_2O_4$ -air (ref. 5) are based on the constants of reference 12. The calculated volume compositions presented herein thus show a little more  $NO_2$  than would be obtained from the equilibrium constants of reference 14. The fuel composition would be less affected. The fuel composition is further established near the composition limits because here new mixtures were usually prepared and the fuel pressure was measured directly.

Determination of limits. - The tube was first evacuated and purged with the mixture and then the mixture was admitted to the desired pressure. The cameras were started, the spark was fired, and the flame behavior was observed. The pressure after the sparking was also noted. This procedure was repeated until at least two "yes" and two "no" initial pressures were obtained with an acceptable minimum separation of 10 percent or less; "yes" indicates propagation through the full length of tube. The "limit" is a midpoint pressure between the "yes" and the "no". There are several cases where the deviations were larger than the measurement precision. At the high pressure near the composition limits, precision was sometimes sacrificed because the reservoir pressure was depleted rapidly. These larger deviations were acceptable, however, because near the composition limits the pressure limit changes rapidly. For every numerical pressure limit reported, the "yes" and the "no" pressures are also given; thus the precision of each determination can be easily established.

Evaluation of apparatus. - An over-all evaluation of the apparatus was made using propane-air (moisture and carbon dioxide free) mixtures; the results are shown in figure 2. In this figure, the results from this apparatus are compared with those obtained for the same fuel-oxidant combination by other operators with other equipment. The agreement is acceptable. The lean limits are perhaps a little on the rich side, but at stoichiometric the pressure limit is lower. The rich limit is somewhat higher near atmospheric pressure than the earlier data compiled in reference 4.

## RESULTS AND DISCUSSION

### Limits of Flame Propagation

The limits of flame propagation of propane and n-pentane in oxides of nitrogen at various subatmospheric pressures are shown in tables I to III and the results are further compared in figures 3 to 5.

Pressure limit as function of percent by weight of fuel. - Propagation pressure limits for the six fuel-oxidant combinations are shown in figure 3 plotted as a function of percent by weight of fuel. The expected roughly U-shaped curves were obtained. The region of flame propagation for each combination is within the "U" of the respective curve. The presence of lobes on the curve was less apparent for the hydrocarbon-NO mixtures than for the mixtures containing  $N_2O_4$ . On the basis of percent by weight, the limits for NO are more lean than those for  $N_2O_4$ . The lean limits for the fuels with NO- $N_2O_4$  are nearly coincident with those with  $N_2O_4$ ; the rich limits are intermediate between those with NO and  $N_2O_4$ . In the stoichiometric region, propagation with both fuels in  $N_2O_4$  occurred at lower pressures than in NO. For the NO- $N_2O_4$  mixtures, the propagation pressure was intermediate between those for NO and  $N_2O_4$ . The results at the lower pressures are largely a function of quenching. They show, as was expected (ref. 2), that quenching affects flames supported by NO more than those by  $N_2O_4$ .

Pressure limit as function of percent by volume of fuel. - Figure 4 shows the limits for the same combinations plotted as a function of percent fuel by volume computed at the limiting pressure. Because of the dissociation of  $N_2O_4$  to  $NO_2$ , the curves for mixtures containing  $N_2O_4$  show a shift to lower percentages by volume of fuel at low pressures, since the oxidant occupies more volume as pressure is reduced. This makes the lean-limit curve appear to be nearly vertical, especially for the mixtures containing  $N_2O_4$  alone. The stoichiometric fuel content, nevertheless, increases as the vertical line is descended. Both propane and *n*-pentane in  $N_2O_4$  tended to explode more violently than usual when ignited near the lean limit at the higher pressures. This was the only region in any of the mixtures where strong explosions near limiting conditions were found.

Estimation of composition limits of the fuel-NO- $N_2O_4$  mixtures. - It was found that linear interpolation described fairly well the limits of the ternary mixtures with respect to the separate oxidants. The dashed curves (fig. 4) were computed from the relation

$$L_{NO-N_2O_4} = \frac{L_{NO} P_{NO} + L_{N_2O_4} (100 - P_{NO})}{100}$$

where

$L_{NO-N_2O_4}$ , composition limits by volume of NO- $N_2O_4$ , NO, and  $N_2O_4$ ,  
respectively  
 $L_{NO}$ ,  $L_{N_2O_4}$

$P_{NO}$  percent by volume of NO in oxidant computed at limiting pressure

The calculated limits lie outside the experimental curves. On an over-all basis, the lean-limit curves give the best fit with a maximum deviation of 0.6 percent. The rich-limit experimental curves are more lobed and show a wider deviation. The deviation is less than 2 percent, however, except for propane at the low pressures. However, when the deviation is computed on the basis of fuel percentage, the maximum deviation is then about 9 percent of the fuel for both the lean and the rich limits. The n-pentane mixtures usually show smaller deviations than the propane mixtures.

Stoichiometric effects. - The wide variations in the behavior of the limits (figs. 3 and 4) are largely the result of difference in stoichiometry. A better comparison can be made using the parameter:

$$F/(F + F_0)$$

where

F fuel in mixture

F<sub>0</sub> fuel that could be completely burned by the oxidant  
in the mixture

This parameter places all possible fuel-oxidant mixtures between 0 and 1; that is, 0 containing no fuel, 1 containing no oxidant, and 0.5 being stoichiometric. As is shown by figure 5, the curves for all the combinations are fairly similar except for the lean limits of both the hydrocarbons with NO which are lower. The limits of n-pentane are somewhat more fuel rich than propane, especially the rich limits. For these data,

the limits occur roughly at equivalence ratios  $\frac{\text{fuel/oxidant}}{(\text{fuel/oxidant})_{\text{stoich}}}$  of

1/3 and 3 or at  $F/(F + F_0)$  values of 0.25 and 0.75. This approximation does not apply for all fuel-oxidant combinations, however. The following table shows some examples:



Fuel-oxidant combination	Lean		Rich		Source
	F/(F + F <sub>O</sub> )	Fuel equiva- lence ratio, <div><math>\frac{F/O}{(F/O)_{\text{stoich}}}</math></div>	F/(F + F <sub>O</sub> )	Fuel equiva- lence ratio, <div><math>\frac{F/O}{(F/O)_{\text{stoich}}}</math></div>	
Propane-NO	0.19	0.23	0.72	2.6	Fig. 5
<u>n</u> -Pentane-NO	.20	.25	.76	3.1	
Propane-N <sub>2</sub> O <sub>4</sub>	.26	.36	.73	2.6	
<u>n</u> -Pentane-N <sub>2</sub> O <sub>4</sub>	.27	.38	.79	3.7	
Propane-NO-N <sub>2</sub> O <sub>4</sub>	.27	.37	.71	2.4	
<u>n</u> -Pentane-NO-N <sub>2</sub> O <sub>4</sub>	.27	.37	.77	3.3	
Propane-O <sub>2</sub>	0.11	0.12	0.87	6.7	Ref. 4
	.10	.12	.84	5.4	Ref. 4
Propane-Air	.35	.55	.72	2.6	Fig. 2
Pentane-Air	.35	.55	.76	3.2	Ref. 4
Hydrogen-O <sub>2</sub>	0.020	0.020	0.92	11.5	Ref. 4
Hydrogen-Air	.094	.103	.88	7.0	Ref. 4

Some significant observations may be made by comparing the limit data for the oxides of nitrogen with other atmospheres containing oxygen and nitrogen as shown in figure 6. The composition limits of the oxides, extrapolated to 1 atmosphere, were recalculated to represent what they would be if the oxides were completely decomposed to molecular oxygen and nitrogen before propagation. The data of reference 5 for the system propane-N<sub>2</sub>O<sub>4</sub>-air were treated in the same manner. All these data are plotted in figure 6 along with data for propane in air and oxygen, and mixtures containing air and nitrogen. The experimental limits for the three propane - nitrogen oxide combinations shown are appreciably narrower than the interpolated limits for the equivalent mixtures of propane with O<sub>2</sub> and N<sub>2</sub>.

From the practical standpoint, it may be desirable to decompose the oxides as much as possible before trying to burn hydrocarbons in them, particularly if fuel-rich mixtures are to be used.

Estimated flame temperatures at lean limits. - The relative stability of NO is well-known. In terms of combustion parameters this stability has been demonstrated by its low flame speeds and large quenching diameters (ref. 2). If the combustion temperatures at the lean limits herein are calculated assuming no dissociation of NO, some interesting inferences can be made. The following table shows these temperatures for the hydrocarbons in the oxides and also the lean-limit combustion temperatures for the same hydrocarbons in air:

Oxidant	Fuel	Temperature, °K
NO	Propane	2059
	<u>n</u> -Pentane	2078
NO-N <sub>2</sub> O <sub>4</sub> (1:3 by wt)	Propane	1568
	<u>n</u> -Pentane	1627
N <sub>2</sub> O <sub>4</sub>	Propane	1381
	<u>n</u> -Pentane	1501
Air (ref. 15)	Propane	1656
	<u>n</u> -Pentane	1758

For the mixtures containing N<sub>2</sub>O<sub>4</sub>, it was assumed that all excess NO<sub>2</sub> was dissociated to NO and O<sub>2</sub> and that none of the oxygen reacting with the fuel came from the NO. Thus, the NO behaved only as a diluent. It is readily seen that the temperatures for the mixtures containing N<sub>2</sub>O<sub>4</sub> and NO-N<sub>2</sub>O<sub>4</sub> are lower than those with air. Furthermore, for the same oxidants, n-pentane gives higher temperatures than propane as is the case with air. In the NO-N<sub>2</sub>O<sub>4</sub> mixtures as well as in the N<sub>2</sub>O<sub>4</sub> mixtures, NO does not have to dissociate to supply oxygen to support combustion; thus the limiting combustion temperatures for the N<sub>2</sub>O<sub>4</sub> and the NO-N<sub>2</sub>O<sub>4</sub> mixtures are lower than those for NO. In the mixtures containing only NO the limiting combustion temperatures are higher, as expected, since a higher temperature would be required to decompose NO at a rate sufficient to support combustion. These data support a supposition that NO in the presence of excess oxygen behaves mostly as a diluent at the fuel-lean flammability limit.

#### Supplementary Data

Appearance of flame. - Most of the reactions were strongly luminous flames. These flames usually were about the same diameter as the tube. The top portion was either hemispherical or ellipsoidal in shape and had a trail which was pointed, that is, they looked like an inverted teardrop ascending the tube; these will be called teardrop-shaped flames. In a few cases the trail was absent, and these flames will be called dome shaped. A few flames did not have a trail and were not dome shaped but looked like dunce caps and ascended the tube with the point facing up. These will be referred to as cones. Other flames filled all or a large portion of the tube and will be called streak- or spear-shaped flames.

The color and luminosity of the flames varied with mixture composition. Flames in NO were usually bright white with yellow showing in fuel-lean and yellow or pink in fuel-rich mixtures. They were more bluish near stoichiometric. The pink color may be an indication of CN (cyanogen) emission observed in reference 2.

The flames in  $N_2O_4$  were orange in the fuel-lean and stoichiometric regions, but the reactions were nonluminous in the more fuel-rich mixtures. These nonluminous reactions were best observed when the tube was illuminated by external light. The reaction zone was about the same shape as a dome-shaped flame and had a yellowish-green color, which contrasted with the red color of the nitrogen dioxide. These were quite often followed by a mist in the tube, which sometimes condensed to rivulets of nonvolatile liquid.

Flames in NO- $N_2O_4$  were orange for fuel lean and stoichiometric. As the mixture became more fuel rich, nonluminous reactions occurred, but near the fuel-rich limits, however, the flames were again luminous. Two types of flame shapes were observed, teardrop and rapid-spear.

Modes of flame propagation. - The luminous flames usually propagated in a lunging or halting manner and the apparent velocities were variable. Some examples of flame-travel-against-time plots, taken from motion-picture films, are shown in figure 7. In general, the apparent velocities were highest at the start and became slower as the flame ascended the tube. This same effect has been observed in closed tubes with other combinations (refs. 16 and 17, e.g.). Some observations of apparent flame speed were made in which the maximum velocity of the first flame lunge was taken as being least affected by uncontrolled variables. The data were not consistent but they suggest that (1) luminous flames travel faster in the rich mixtures, at least for the 1:3 by weight NO- $N_2O_4$  blend, and (2) the velocities decrease as the extreme rich and lean mixtures are approached.

Whether or not pressure itself affected the flame speed is debatable. The data of reference 2 show a weak trend for flame velocities of hydrocarbons to increase with pressure in NO and decrease with pressure in  $N_2O_4$ . It seems likely that (1) the velocities of the rich mixtures are higher because of higher concentrations of H radical and (2) the velocities fall off in the extreme rich and extreme lean mixtures because of lower flame temperatures.

These observations, however, do not apply to the nonluminous reactions, which are considerably slower. These seem to represent a different kind of mechanism.

Flame arrests. - As is shown by the examples in figure 7, the flames often suddenly decrease velocity or come to a halt during the propagation

up the tube. In some cases, this effect was very striking; the dome of the flame became flat, seeming to strike an invisible wall in the tube. Flame arrests have been observed in other mixtures in closed tubes; for recent examples, see references 16 and 17. A compilation of the positions of the first arrest for about 40 propagations showed that they occurred over a range of lengths covering the upper three-fourths of the tube. Although not apparent from figure 7, most of the arrests occurred at approximately one-third and two-thirds of the tube length and only a few were at one-half the length. Although significance of this occurrence is difficult to appraise with the data available, the fact that the arrests occur preferentially at certain spots in the tube may possibly be associated with standing sonic waves driven by the flame. An analysis of this is complicated because various oscillation modes are possible and the pattern may be shifted by unequal temperature in the tube during propagation.

Photographs by Hahnemann, Neubert, and Ehert presented in reference 3 show that flat flame fronts such as occur during flame arrests can be obtained in an externally driven oscillating tube. If standing sonic waves were produced in the experiments herein, they were undetectable by the pressure pickup at the limiting conditions. The amplitude of the waves would therefore have to be less than about 5000 dynes per square centimeter. The energy required to set up a wave of this magnitude is infinitesimal compared with the energy released by the flame even at limiting conditions. It is well-known, however, that sound waves affect diffusion flames, probably by triggering vortices in the flow (ref. 3, e.g.). During flame propagation in a closed tube, there is some transport of the gases, and it is conceivable that vortex triggering could occur. Schlieren photographs of references 16 and 17 show considerable small-scale turbulence in the vicinity of flame arrests and there is evidence (ref. 18) that small-scale turbulence will inhibit a flame. It may be possible that flame arrests are caused by standing waves.

The nonluminous reactions, however, were steady and did not show arrests. This could be due either to a different chemical mechanism or to the fact that the nonluminous propagation was appreciably slower and perhaps did not offer an opportunity for the alleged vortex-triggering mechanism.

Pressure effects resulting from flame propagation. - Rapid-response records show that pressure rise usually coincided with the advance of flame front. If high-frequency standing oscillations existed, they were usually below the noise level in the recording apparatus. Flames were usually quiet. A few noisy flames with accompanying high-frequency pressure vibrations were observed but these were at pressures considerably above the limiting pressures.

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"Equilibrium" pressures after propagation were measured primarily as a secondary check on propagation. The equilibrium pressure rise caused by a flame that had been quenched was usually decidedly less than for full propagation. The rise was not proportional to the travel distance.

Although these measurements were not made as a primary parameter and may not have been made at true equilibrium with respect to either composition or ambient temperature, they do exhibit some interesting trends and are therefore shown in figure 8. High pressure rises were often obtained in an extreme fuel-rich region; this was most consistent for the fuels burning in NO. This effect was not found in  $N_2O_4$ , but in the mixed oxides the pressures were both high and low near the rich limit. The high pressures seem to be the result of luminous teardrop-shaped flames. The nonluminous flames in  $N_2O_4$  and also spear-shaped flames in the mixed oxides did not produce as high a pressure. These observations indicate that a large quantity of gas is generated when excess hydrocarbons burn in the teardrop-shaped flame, particularly those in NO.

Two distinct combustion reactions are shown to occur with rich hydrocarbon mixtures in oxides of nitrogen. Nonluminous reactions, favored in  $N_2O_4$ , produce nonvolatile liquids; while strongly luminous reactions, favored in NO mixtures, produce gases. Further study of these reactions and their products may be of both practical and speculative interest.

#### SUMMARY OF RESULTS

Flame propagation limits at subatmospheric pressures were measured for propane and *n*-pentane, individually, in nitric oxide NO, nitrogen tetroxide  $N_2O_4$ , and the nearly equimolar mixture of the two. Observations were also made of the appearance of the flames and their apparent velocities and pressure effects. It was found that:

1. All the combinations had a region of flame propagation which could be ignited by a 60-cycle, 25,000-volt spark.
2. On a volume or weight basis, the limits of the hydrocarbons with  $N_2O_4$  were higher and wider than with NO.
3. The minimum pressures at which propagation in the 2-inch tube would occur was less for fuel- $N_2O_4$  than fuel-NO mixtures.
4. The limits at which flames will propagate in the NO- $N_2O_4$  mixtures were intermediate with respect to percent by volume fuel and to minimum pressure. The volume composition limits of this mixture over a range of subatmospheric pressures were predicted fairly well by linear interpolation.

5. The composition limit behavior was largely a function of stoichiometry. The limits for all the combinations occurred roughly at equivalence ratios of 1/3 and 3. On a stoichiometric basis, NO mixtures had the lowest lean limits.

6. Estimated flame temperatures at the lean limit were appreciably lower for the  $N_2O_4$  and the NO- $N_2O_4$  mixtures than for the NO mixtures, and were about the same as lean-limit temperatures of fuels in air.

7. The limits of the oxides in propane at 1 atmosphere are narrower than the interpolated limits for equivalent mixtures of molecular nitrogen and oxygen, when the composition of the propane-oxide mixtures are calculated assuming complete decompositions of oxides before propagation.

8. The flames were usually strongly luminous. Nonluminous reactions, however, occurred in the fuel-rich  $N_2O_4$  and NO- $N_2O_4$  mixtures at low pressures. In the fuel- $N_2O_4$  mixtures, particularly, the nonluminous reactions produced nonvolatile liquids. Strongly luminous flames in the fuel-rich NO and NO- $N_2O_4$  mixtures, however, produced a considerable quantity of gas.

9. The luminous flames were characterized by varying velocities and flame arrests. The apparent velocities were usually greater when flames were in the lower part of the tube. The arrests occurred preferentially at certain spots in the tube.

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National Advisory Committee for Aeronautics  
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TABLE I. - FLAME PROPAGATION LIMITS OF HYDROCARBONS WITH NITRIC OXIDE, NO

16

Series	Composition, percent by weight		Mixture comparison parameter, fuel/(fuel + fuel equivalent of oxidant)	Initial conditions at flame propagation limit						Flame description	
	Fuel	NO		Temperature, °C	Composition, percent by volume		Pressure, mm Hg				
					Fuel	NO	Consistent propagation, "yes"	Consistent non-propagation, "no"	Accepted limiting pressure		
Fuel, propane											
1	28.9	73.1	0.715	25	20.0	80.0	385	383	384	White teardrop, - 5 by 25 cm	
	18.1	81.9	.601	26	15.1	84.9	106	103	104	Bright white teardrop	
	13.0	87.0	.504	28	9.2	90.8	101	90	98	Blue-white teardrop, - 5 by 25 cm	
	3.1	96.9	.180	20	2.11	97.89	---	682	---	Yellow flame lunged up about 1/4 of tube	
2	26.1	71.9	0.728	24	21.0	79.0	---	648	---	White cone shot part way up	
	23.3	76.7	.873	26	17.1	82.9	196	180	193	Bright white teardrop, pink mantle; hesitated twice	
3	25.7	74.3	0.702	22	19.1	80.9	290	280	285	Pink teardrop	
	22.6	77.4	.665	25	18.6	81.4	133	123	128	Blue-white teardrop, pink mantle; - 5 by 25 cm	
	21.0	79.0	.644	27	15.3	84.7	150	145	148	Blue-white teardrop, - 5 by 30 cm	
	17.7	82.3	.594	28	12.8	87.2	122	117	120	White-blue teardrop, - 5 by 30 cm	
	16.4	83.6	.571	28	11.8	88.2	100	91	98	Blue-white teardrop, - 5 by 35 cm	
	15.0	85.0	.545	27	10.7	89.3	95	91	93	White-blue teardrop, - 5 by 50 cm	
	12.9	87.1	.502	25	8.2	90.8	95.3	94.6	95	Blue-white teardrop, - 5 by 30 cm	
	10.9	89.1	.454	24	7.7	92.3	100	96	98	Blue-white teardrop, bright white cone, pink trail, - 5 by 37 cm	
	10.0	90.0	.431	25	7.0	93.0	101	96	99	Blue-white teardrop, white trail, - 5 by 30 cm	
	9.3	90.7	.412	25	6.8	93.6	110	102	106	Blue-white teardrop, bright white crown, yellow-white trail, - 5 by 30 cm	
	8.6	91.4	.391	28	6.0	94.0	107	106	106	White teardrop, yellow-white trail, - 5 by 30 cm	
	7.2	92.8	.346	23	5.0	95.0	135	125	130	Blue-white teardrop, yellow-white crown and trail, unsteady, - 5 by 30 cm	
	4	27.7	72.3	0.723	25	20.7	79.3	858	667	---	Yellow-white teardrop shot 2/3 up tube
		20.7	79.3	.641	23	15.1	84.9	142	140	141	Teardrop, bright white center, bluish mantle, hesitated at midpoint, - 5 by 30 cm
		7.2	92.8	.346	22	5.0	95.0	138	131	134	Yellow-white teardrop, - 5 by 30 cm. NO <sub>2</sub> formed.
		6.3	93.7	.313	26	4.4	95.6	165	158	162	White teardrop, yellowish mantle. Delayed formation of NO <sub>2</sub> .
3.2		96.8	.184	26	2.2	97.8	683	500	532	Bright white teardrop, wavering yellow trail, - 5 by 45 cm	
Fuel, n-pentane											
1	37.5	62.5	0.800	25	20.0	80.0	---	582	---	Orange cone went 10 cm	
	33.0	67.0	.766	24	17.0	83.0	---	560	---	Bright yellow-white teardrop flashed part way	
	28.1	71.9	.722	28	14.0	86.0	479	433	456	Yellow-white teardrop, steady, - 5 by 60 cm	
	22.9	77.1	.684	27	11.0	89.0	146	134	140	Brilliant blue-white egg (5 by 10 cm) with long narrow tail, steady	
	17.3	82.7	.633	26	8.0	92.0	133	124	129	Similar, except longer tail and hesitated part way up	
	13.1	86.9	.600	26	5.9	94.1	132	128	130	Similar to above, gave audible rattling sound	
	9.1	90.9	.559	27	4.0	96.0	148	140	144	Bright blue-white teardrop with yellow streaks	
	6.9	93.1	.530	24	3.0	97.0	169	156	163	Bright white teardrop, yellow tip on tail, halted part way up, - 5 by 35 cm	
	4.7	95.3	.447	26	2.0	98.0	300	288	294	Bright white teardrop, yellow tail, - 5 by 35 cm	
	2.4	97.6	.140	24	1.0	99.0	---	578	---	Yellow flame up 35 cm	
2	31.4	68.6	0.733	24	18.0	82.0	688	530	608	Bright orange-white teardrop grew larger, whiter, and brighter toward top	
	29.9	70.1	.740	25	15.1	84.9	535	496	510	Bright orange-white teardrop nearly extinguished part way up, - 5 by 60 cm	
	25.6	74.4	.696	25	12.5	87.5	168	158	163	Bright blue-white teardrop, - 5 by 30 cm	
	13.1	86.9	.600	25	5.9	94.1	134	131	133	As above, - 5 by 35 cm	
	3.6	96.4	.199	26	1.51	98.49	498	497	497.5	Very bright white teardrop. Condensation remained.	

\*Propagation occurred once at this pressure.

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TABLE II. - FLAME PROPAGATION LIMITS OF HYDROCARBONS WITH NITROGEN TETROXIDE,  $N_2O_4$ 

Series	Nominal mixture composition, percent by weight		Mixture comparison parameter, Fuel/(fuel + fuel equivalent of oxidant)	Initial conditions at flame propagation limit							Flame description
	Fuel	N <sub>2</sub> O <sub>4</sub>		Temperature, °C	Equilibrium composition, percent by volume			Pressure, mm Hg			
					Fuel	N <sub>2</sub> O <sub>4</sub>	NO <sub>2</sub>	Consistent propagation, "yes"	Consistent non-propagation, "no"	Accepted limiting pressure	
Fuel, propane											
1	8.1	91.9	0.315	25	10.3	21.8	67.8	56	51	54	Bright orange teardrop, light orange trail, = 5 by 35 cm, jerky Faint orange teardrop, bright orange crown, = 5 by 12 cm Similar to above, = 5 by 30 cm, jerky Nonluminous teardrop or dome Nonluminous
	14.3	85.7	.488	25	16.4	10.3	73.4	24	23	23.5	
	20.2	79.8	.589	25	24.0	14.9	61.1	51	38	45	
	26.8	73.2	.657	24	31.9	15.2	52.9	88	45	57	
	33.5	66.5	.725	25	43.3	26.7	31.0	326	277	302	
2	6.6	93.4	0.269	25.5	10.2	46.4	41.4	334	328	330	Bright orange streak, turbulent, spotted, = 50 cm long, flashed back filling tube
4	5.7	94.3	0.240	28	9.3	88.7	34.0	---	594	---	Orange dome went 8 cm Hanging orange dome became steady teardrop with bright crown and light trail, = 5 by 40 cm Light orange teardrop, bright head, dull trail, = 5 by 30 cm Bright orange teardrop, vapor-like trail, = 5 by 30 cm
	6.8	93.2	.275	28	9.8	38.0	52.2	210	184	197	
	8.8	91.4	.330	28	10.2	14.1	75.7	36	33	35	
	10.6	89.4	.383	27	12.3	11.5	76.2	35	17	28	
5	6.3	93.7	0.258	28.5	10.1	64.8	35.4	---	840	---	Orange dome up about 40 cm
6	14.0	86.0	0.459	26	15.8	8.9	78.3	22	17	19	Orange teardrop = 5 by 25 cm Dark orange dome, inside and trail light orange, = 5 by 25 cm Nearly nonluminous dome or teardrop, = 5 by 25 cm Nonluminous, = 25 cm long. Fog remained. Nonluminous, = 25 cm long
	17.0	83.0	.517	26	19.6	11.8	68.8	32	28	30	
	24.0	76.0	.622	24	27.8	12.2	60.0	57	34	36	
	30.2	69.8	.683	25	35.3	13.3	51.1	61	55	58	
	31.2	68.8	.703	25	36.8	14.7	48.4	74	67	71	
7	32.4	67.6	0.714	24	39.8	17.2	43.7	97	90	84	Nonluminous, = 25 cm long. Fog remained. Nonluminous, = 20 cm long. Fog remained.
	32.8	67.1	.718	25	39.8	17.6	42.6	119	100	109	
Fuel, n-pentane											
1	34.7	65.3	0.731	26	26.2	11.4	60.4	48	26	38	Nonluminous, teardrop, = 5 by 15 cm
2	37.2	62.8	0.752	25	33.2	21.1	45.7	115	113	114	Nonluminous teardrop, = 5 by 25 cm, steady propagation Nonluminous teardrop, = 5 by 25 cm, colorless gas remained Teardrop, orange envelope, = 5 by 20 cm
	28.3	71.7	.646	25	21.3	16.0	63.7	87	86	42	
	13.3	84.7	.480	25	11.7	12.9	75.4	28	23	25	
3	38.9	61.1	0.784	26	37.1	28.8	34.0	318	287	302	Nonluminous, dense fog remained Yellow-orange teardrop, colorless gas remained Mild explosion (no glass breakage)
	10.7	89.3	.360	28	8.1	13.8	78.1	35	28	32	
	7.0	93.0	.278	28	7.2	55.8	36.0	579	451	515	
4	41.7	58.3	0.785	27	40.4	30.1	28.5	499	471	485	Nonluminous, dense fog remained Orange flame to middle of tube
	6.8	93.2	.271	28	7.1	59.9	33.0	---	870	---	
5	42.05	57.95	0.787	22	42.8	35.2	22.0	---	546	---	Small nonluminous cone to middle of tube

TABLE III. - FLAME PROPAGATION LIMITS OF HYDROCARBONS WITH NEAR EQUIMOLAR MIXTURE OF NITRIC OXIDE  
AND NITROGEN TETROXIDE, NO-N<sub>2</sub>O<sub>4</sub> (1:3 BY WEIGHT)

Series	Nominal mixture composition, percent by weight			Mixture comparison parameter Fuel/(fuel + fuel equivalent of oxidant)	Initial conditions at flame propagation limit									Flame description
					Temperature, °C	Equilibrium mixture composition, percent by volume					Pressure, mm Hg			
	Fuel	N <sub>2</sub> O <sub>4</sub>	NO <sub>2</sub>								NO	N <sub>2</sub> O <sub>3</sub>	Consistent propagation, "yes"	
Fuel, propane														
1	6.5	89.8	23.7	0.278	25	7.6	24.7	26.7	38.0	3.0	418	362	390	Bright yellow-orange dome (5 by 15 cm), red crown and long yellow-orange trail
	9.8	87.4	22.8	.377	23	10.3	13.0	41.2	34.4	1.0	82	65	74	Dark orange vibrating dome (29 cm), light orange center and 8 cm trail
	14.6	83.8	21.6	.487	24	15.0	10.1	42.1	32.0	.8	83	55	58	Vibrating pointed orange dome, .2 by 20 cm
	18.9	80.6	20.5	.554	26.5	19.8	8.7	39.7	30.4	.8	84	72	78	Nonluminous, .5 by 25 cm, some fog remained
	24.2	56.6	19.2	.640	28.5	25.9	12.7	31.4	28.8	1.2	180	187	188	Brilliant white teardrop with blue core, .5 by 50 cm, some fog
2	5.8	70.9	23.3	0.254	24.5	7.0	28.0	23.1	38.1	3.8	---	570	---	Orange dome went 30 cm
	7.8	69.5	22.9	.313	24	8.2	14.4	41.4	34.9	1.2	89	88	87	Yellow-orange dome (5 by 10 cm), narrow trail lighter
	23.7	57.4	18.9	.832	26	25.8	13.9	30.4	28.8	1.3	189	176	183	Brilliant white streak (spear-shaped)
	26.0	56.4	18.6	.849	28	26.8	12.7	31.3	28.0	1.2	204	191	187	Brilliant white streak
3	8.9	89.7	23.4	0.291	26	7.7	18.9	35.0	38.5	1.9	180	187	173	Orange teardrop with dark orange dome, .8 by 35 cm
	26.1	55.3	18.5	.862	26	28.4	14.3	27.7	28.2	1.4	231	220	226	Brilliant white streak
	28.8	54.8	18.4	.870	27.5	29.0	13.7	28.0	27.9	1.4	244	233	238	Bright white streak
	27.5	54.3	18.2	.877	25	30.4	15.6	24.5	27.9	1.7	298	287	283	Blue-white streak
4	27.8	54.3	17.8	0.882	26.5	30.8	15.1	25.8	27.3	1.5	278	287	272	Brilliant white teardrop, fog remained
	29.4	53.1	17.5	.697	25	33.1	17.4	20.6	26.9	2.0	476	449	463	Orange-white teardrop, ragged trail, .5 by 45 cm. Thick fog remained.
5	32.7	50.7	16.6	0.730	24	35.6	18.9	17.1	26.1	2.4	---	695	---	No ignition
Fuel, n-pentane														
1	6.4	70.3	23.3	0.270	25.5	4.9	26.8	23.1	39.1	4.1	---	572	---	Ragged yellow flame up 1/3 of tube
2	6.9	70.0	23.1	0.286	26	5.0	22.5	32.3	37.7	2.5	331	280	305	Bright yellow, lunging, nearly filled tube
	7.8	69.5	22.9	.309	27	5.4	20.1	35.3	37.1	2.1	218	205	211	Orange cone, yellow trail, unsteady
	9.2	68.3	22.5	.354	27	6.2	14.0	43.2	35.4	1.2	102	88	99	Rapid orange cone, white flashback
	10.7	67.2	22.1	.383	28	7.1	11.0	46.8	34.3	.8	82	59	61	Flickering bright yellow dome
	14.7	64.2	21.1	.482	26	9.8	10.8	45.4	33.3	.8	85	61	63	Bouncing uniformly dull orange dome, .4 by 20 cm
	18.5	61.3	20.2	.552	26	12.4	8.8	46.2	31.9	.6	52	48	50	Smoothly bouncing dull orange dome, .3 by 20 cm
	23.4	57.6	19.0	.623	28	16.0	8.0	44.9	30.5	.6	59	54	55	Nonluminous, diameter < tube, most of NO <sub>2</sub> removed
3	33.2	49.6	17.2	0.730	29	25.1	13.8	29.7	29.9	1.4	243	232	238	Brilliant blue teardrop, "bb buff" sound
	35.6	47.8	16.6	.750	28	24.7	11.9	32.8	29.8	1.1	188	151	158	Steady nonluminous spear, 2/3 diameter of tube
	38.8	46.8	16.3	.781	26	28.0	16.4	24.3	29.6	1.8	359	316	338	Greenish grey-white, filled tube, white fog remained
					27	29.8	17.8	21.2	29.2	2.2	---	519	---	Nonluminous, diameter of tube, quenched abruptly part way up

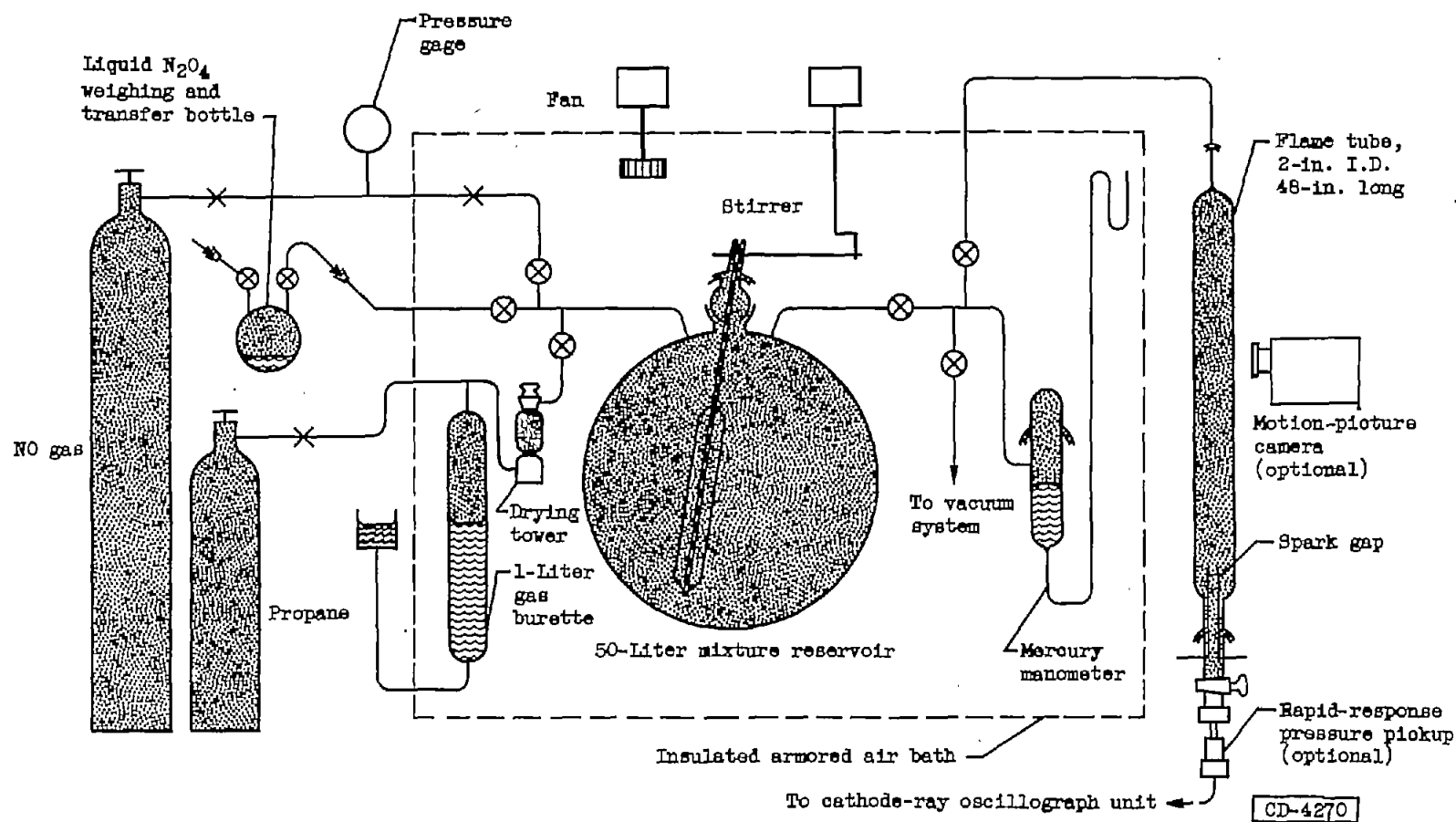


Figure 1. - Diagram of flame propagation apparatus.

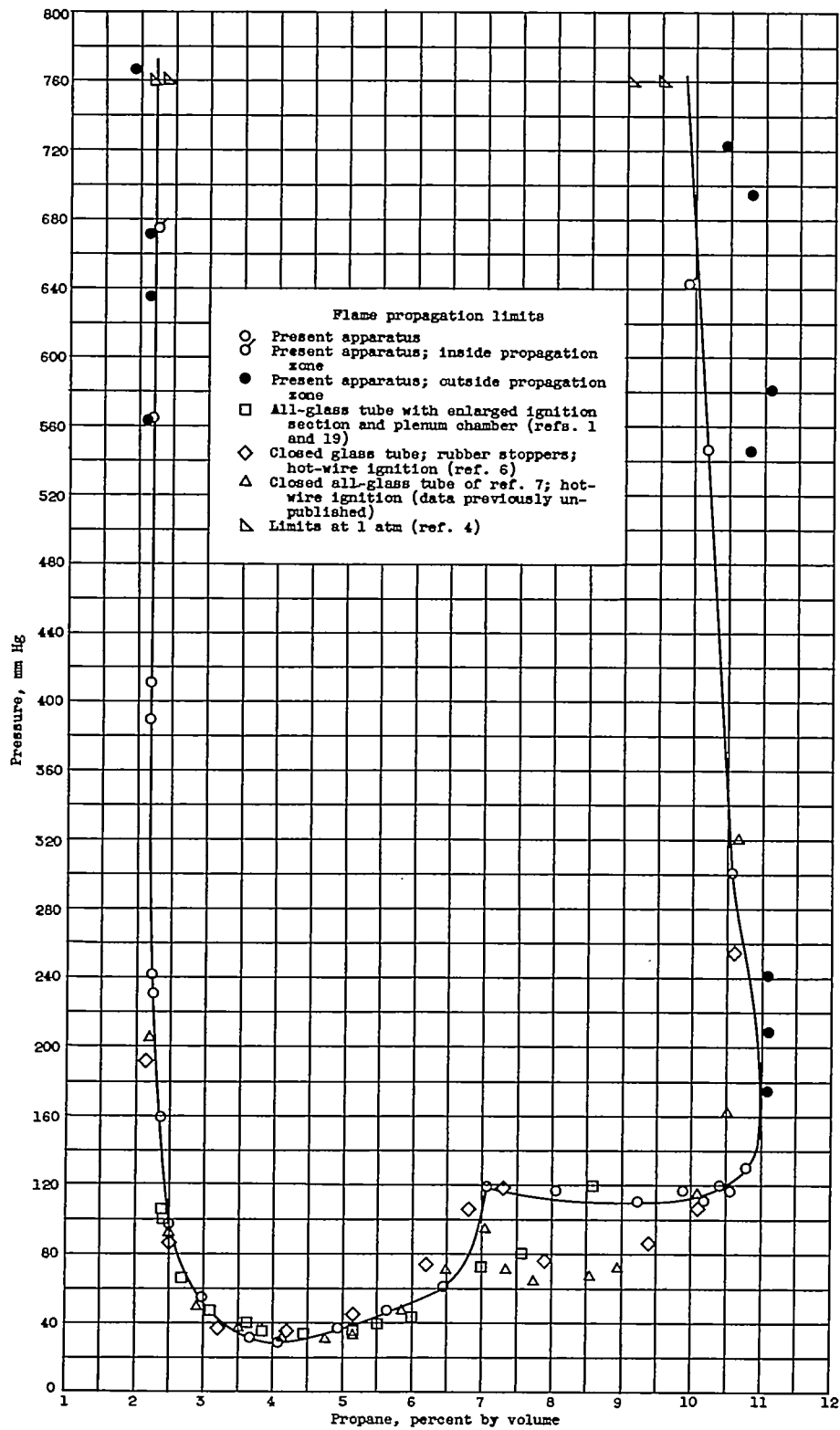
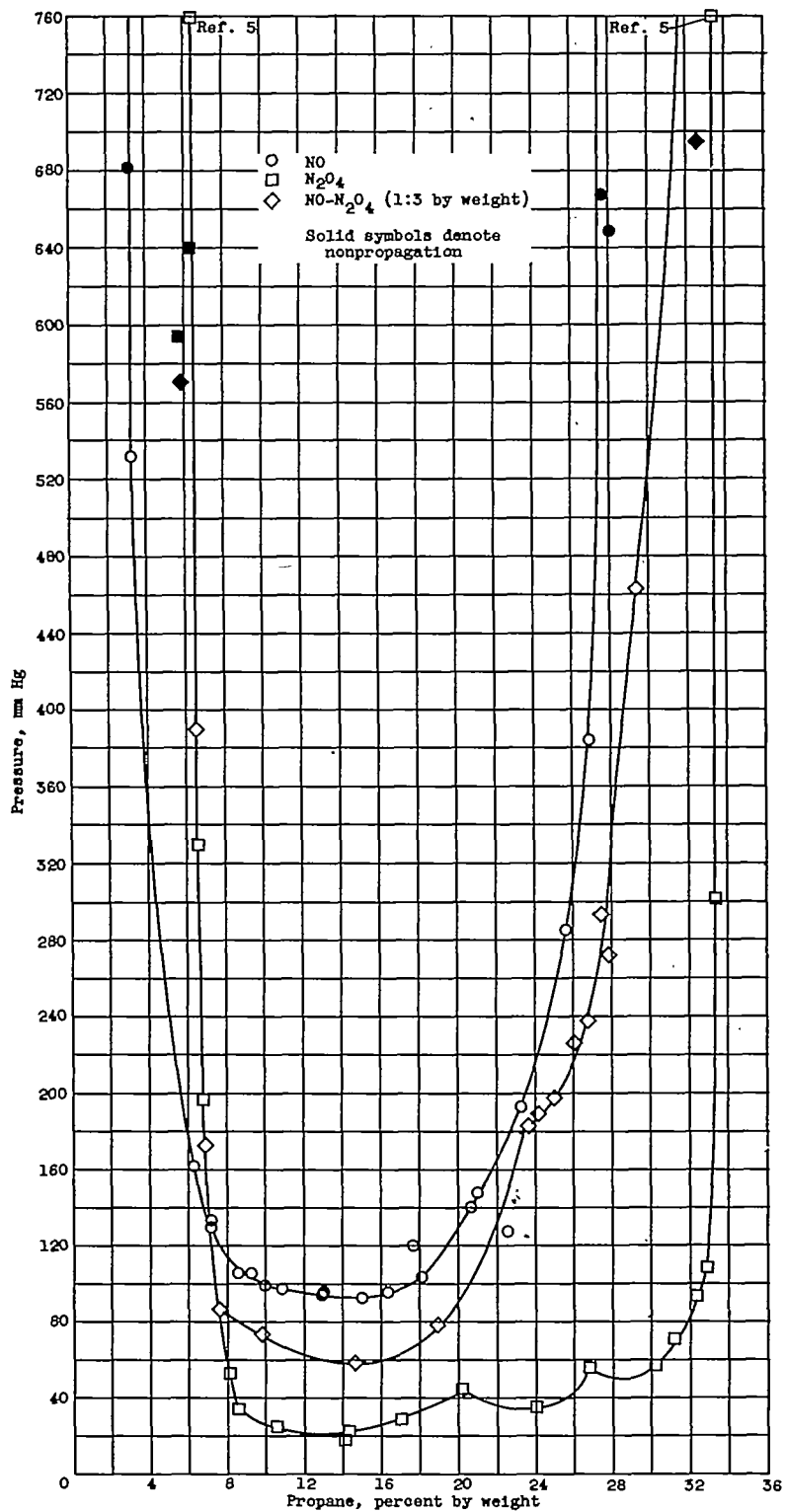


Figure 2. - Comparison of flame propagation apparatus using propane-air mixtures.  
Tube diameter, 2 inches.



(a) Fuel, propane.

Figure 3. - Limiting flame propagation pressure as function of percent by weight hydrocarbon in oxides of nitrogen.

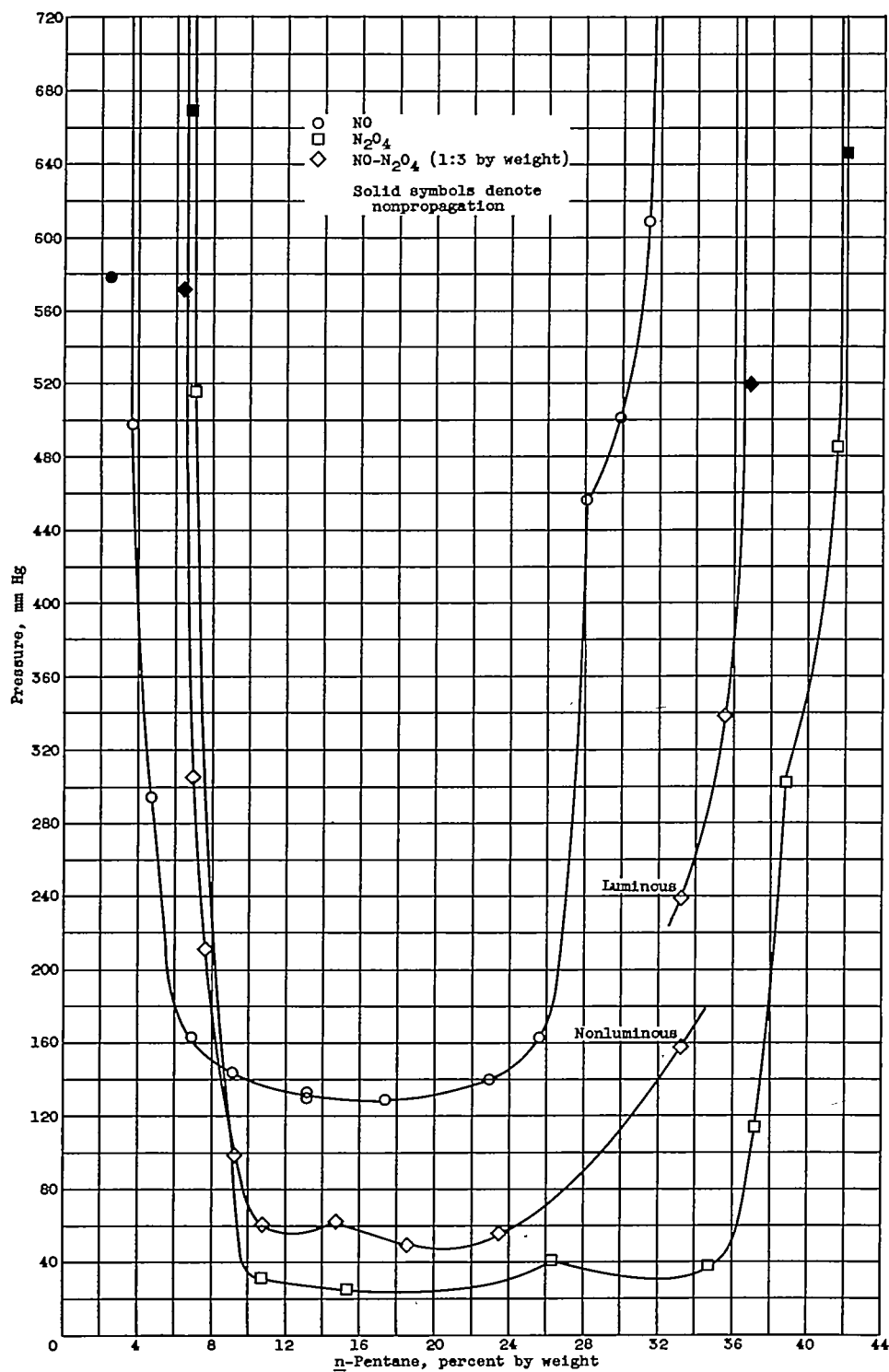
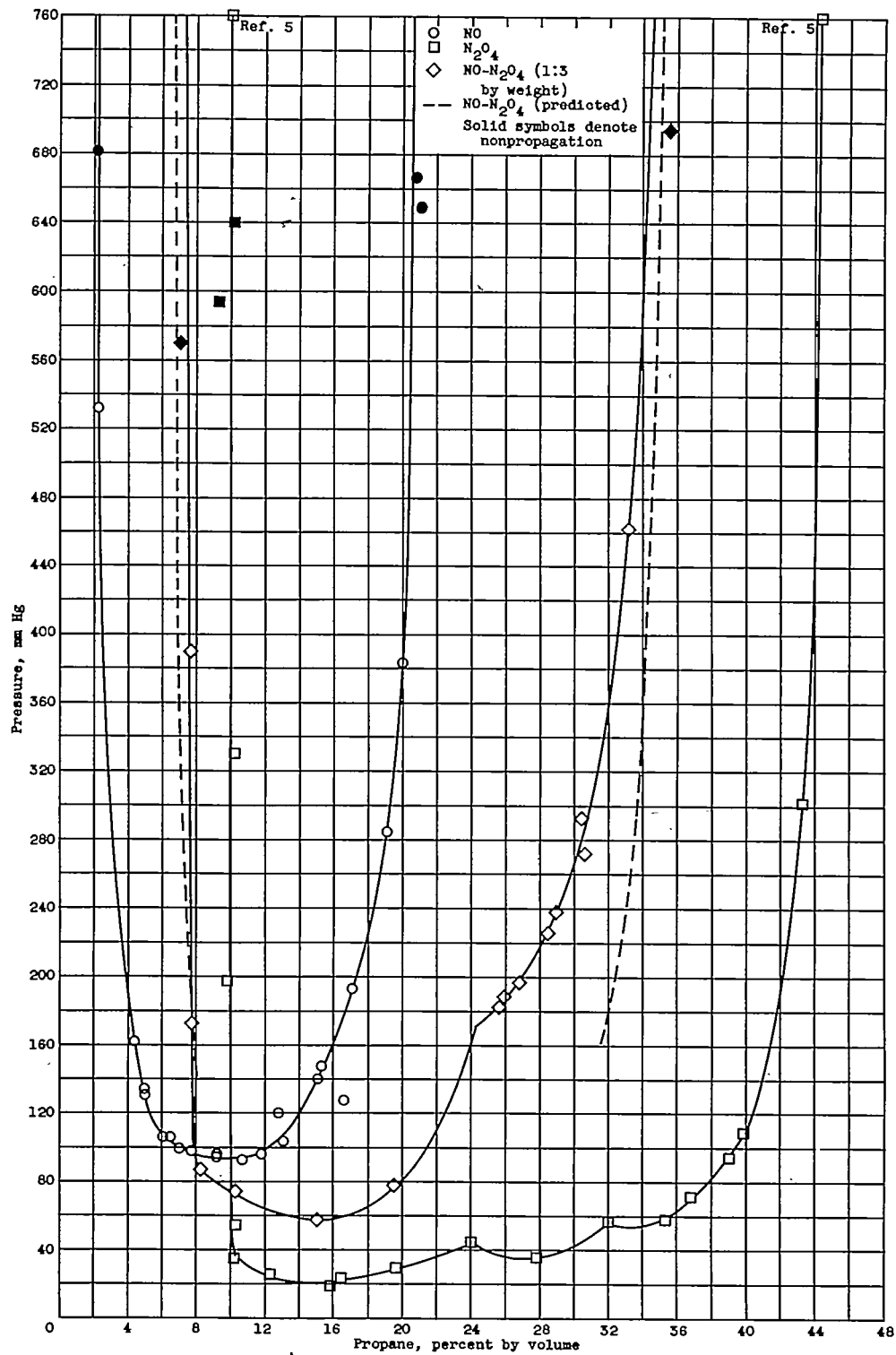
(b) Fuel, n-pentane.

Figure 3. - Concluded. Limiting flame propagation pressure as function of percent by weight hydrocarbon in oxides of nitrogen.



(a) Fuel, propane.

Figure 4. - Limiting flame propagation pressure as function of percent by volume hydrocarbon in oxides of nitrogen. Composition is for equilibrium at limiting pressure.



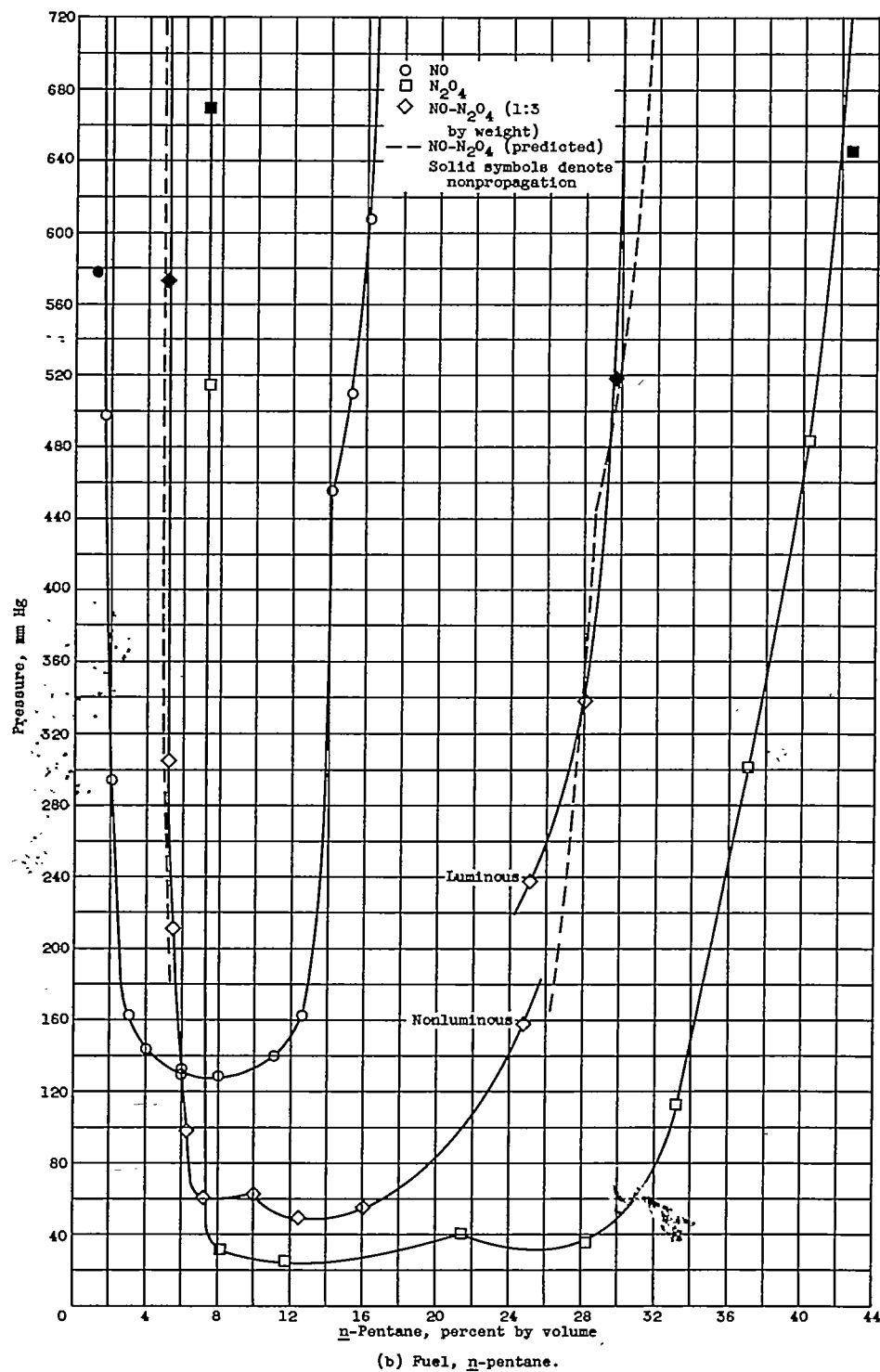
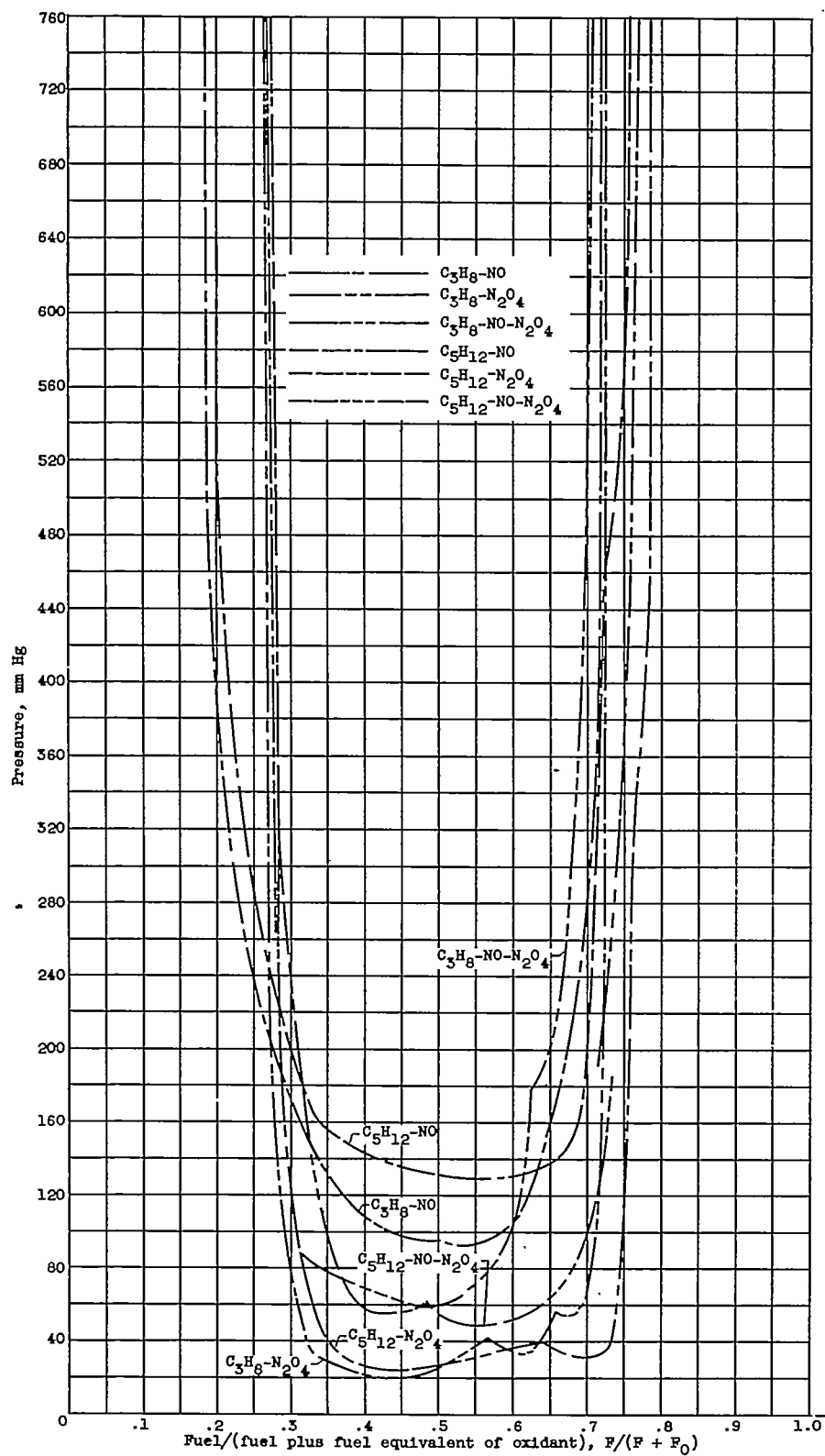


Figure 4. - Concluded. Limiting flame propagation pressure as function of percent by volume hydrocarbon in oxides of nitrogen. Composition is for equilibrium at limiting pressure.



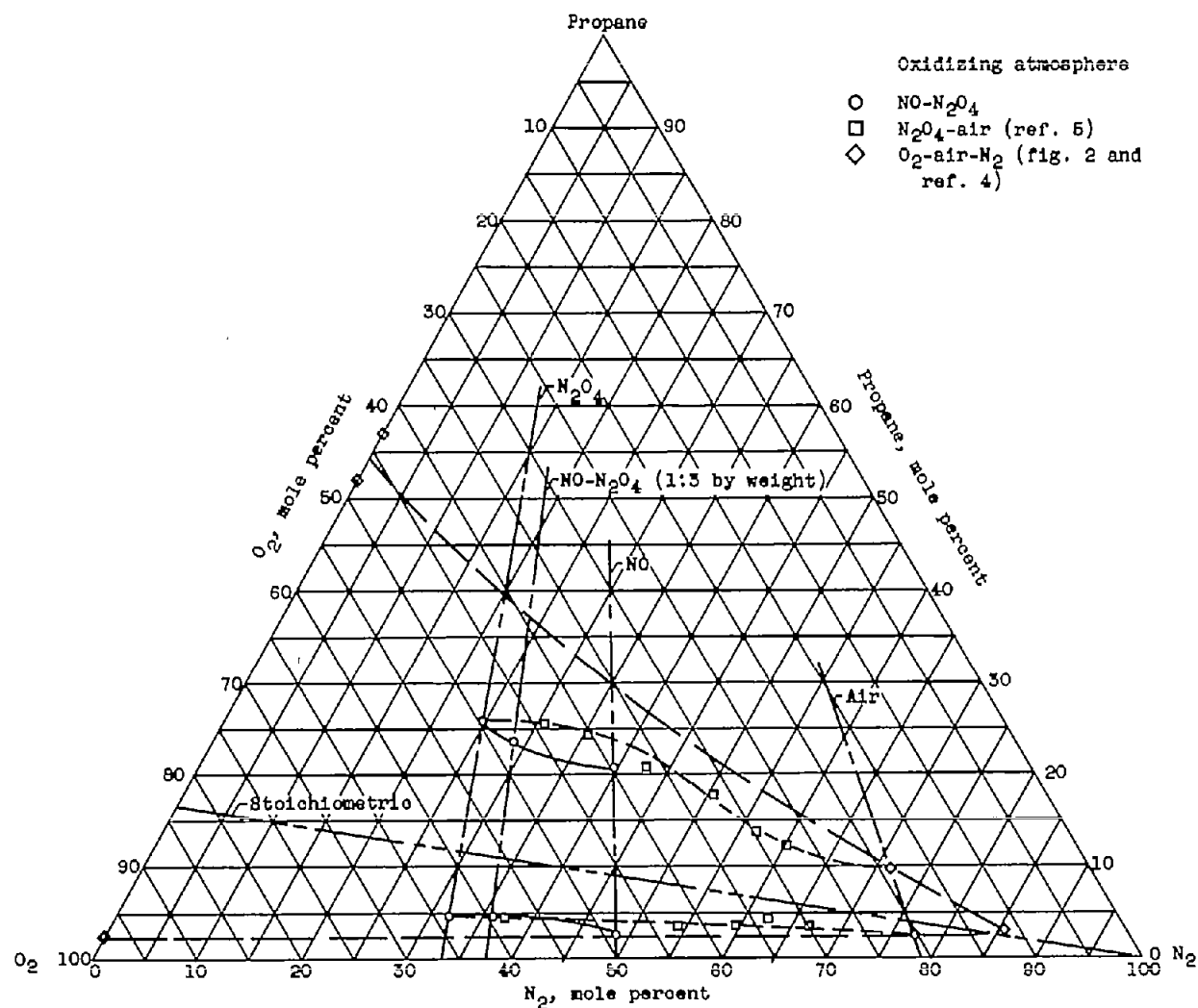
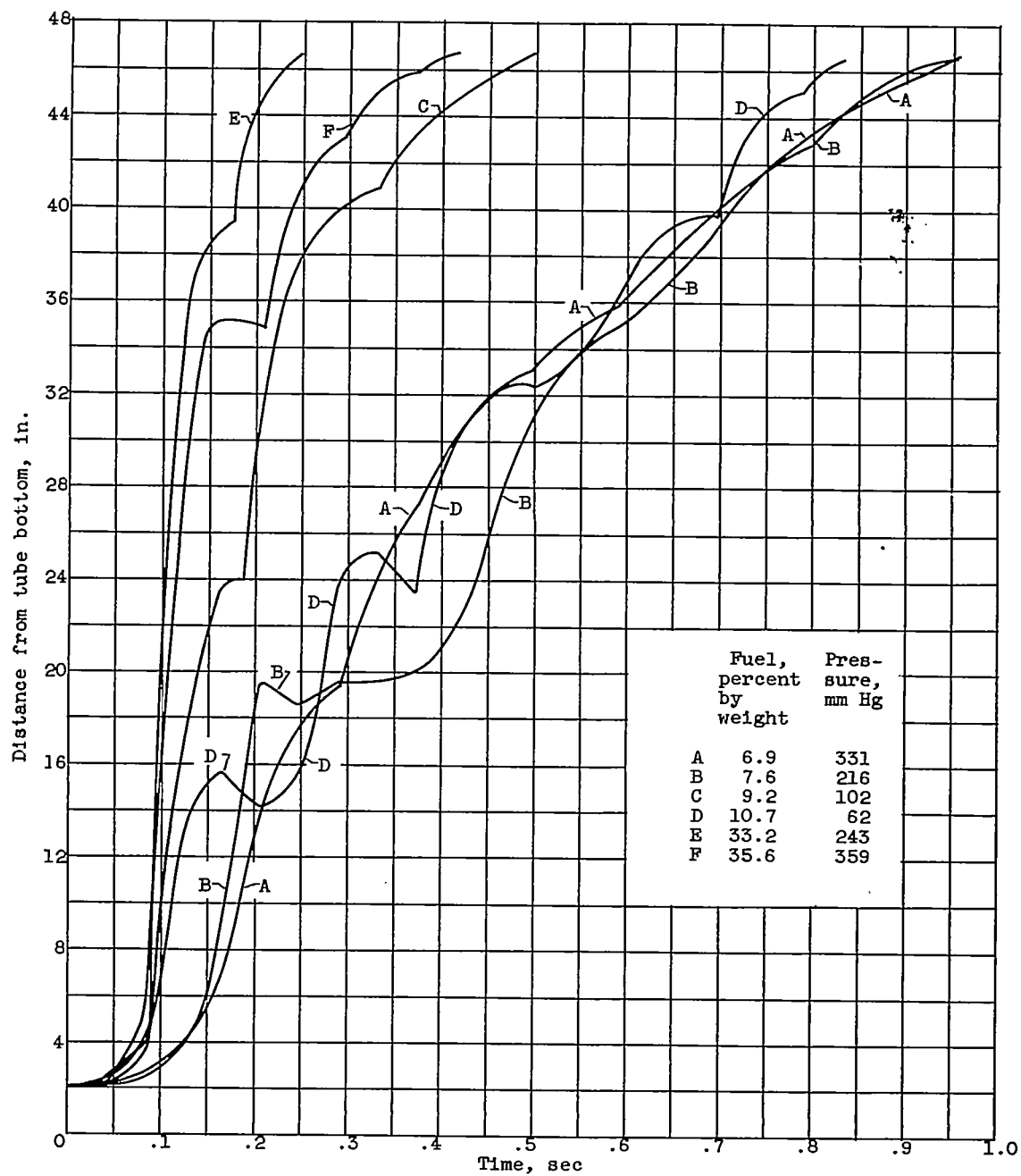
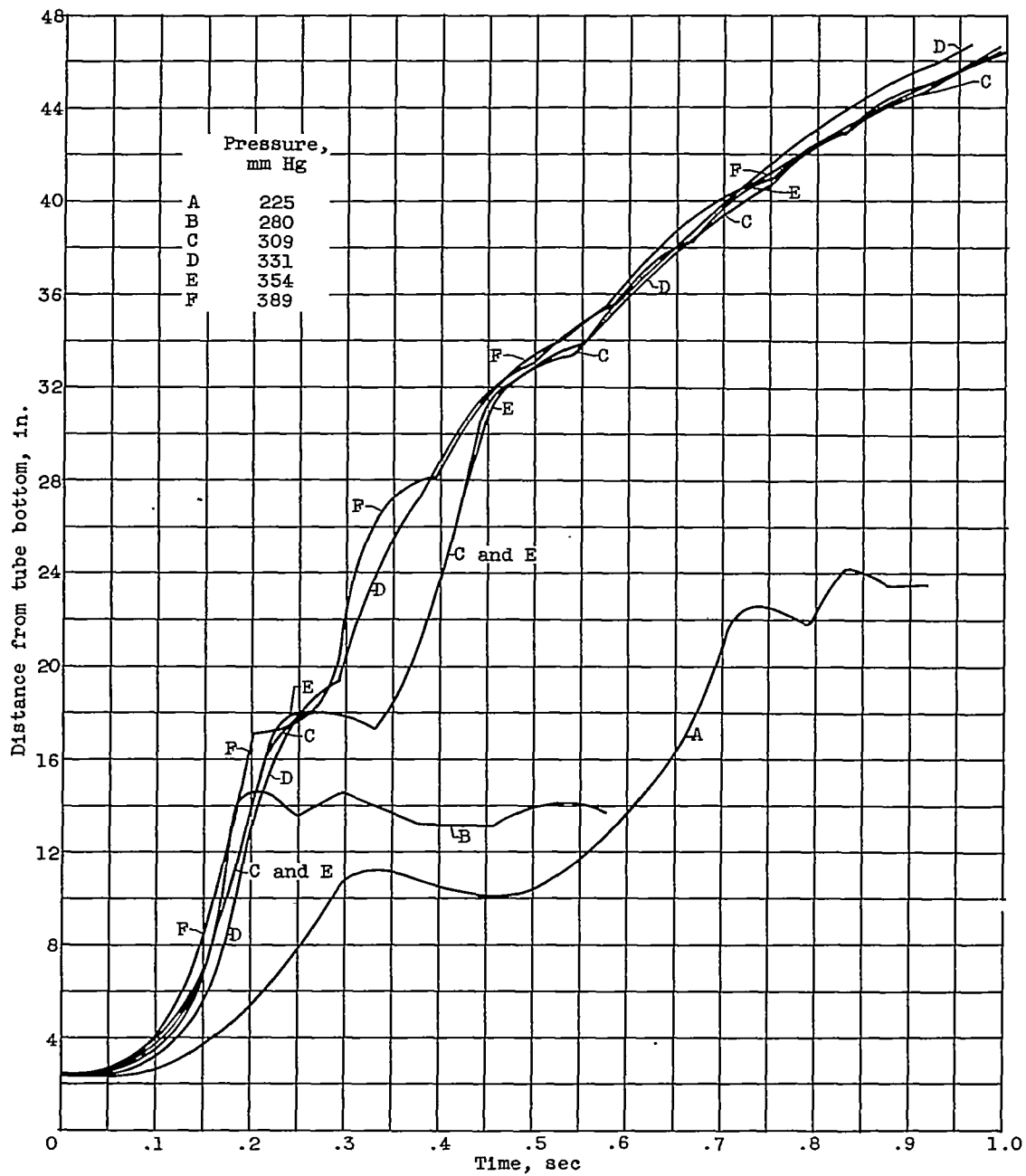


Figure 6. - Comparison of propagation limits of propane in various oxidants of oxygen-nitrogen system. Compositions are what they would be if all oxides were decomposed to oxygen and nitrogen before propagation. Original pressure, 1 atmosphere.



(a) Several mixtures at lowest pressure for consistent propagation.

Figure 7. - Examples of flame-front travel in tube at and near propagation limits. Mixtures, n-pentane in  $\text{NO-N}_2\text{O}_4$ .



(b) Several pressures at constant composition. Fuel, 6.9 percent by weight.

Figure 7. - Concluded. Examples of flame-front travel in tube at and near propagation limits. Mixtures, n-pentane in  $\text{NO-N}_2\text{O}_4$ .

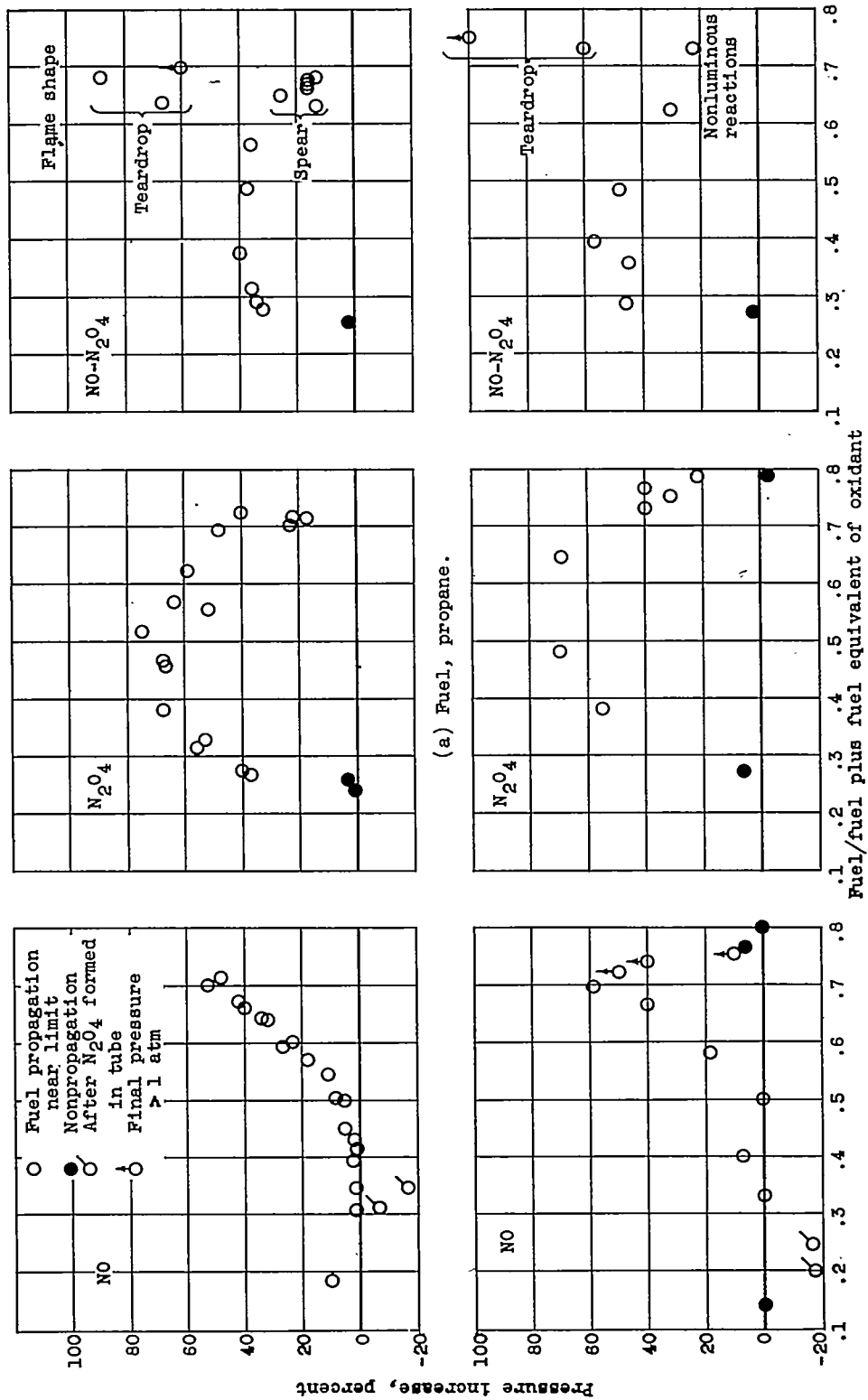


Figure 8. - Pressure increase in tube after firing.